

Carbon Dioxide Sequestration Potential of Calcifying Cyanobacteria

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ABSTRACT

Whittings is an open ocean phenomenon in which CaCO_3 is precipitated from solution by the physiological activity of cyanobacteria, producing a stable bottom sediment. Two strains of cyanobacteria in the genus *Synechococcus* were tested for their carbon sequestration potential through the formation of biomass and CaCO_3 . *Synechococcus* sp. strain PCC 8806 and *Synechococcus* sp. strain PCC 8807 were tested in microcosm studies receiving 2.5 mM HCO_3^- and 3.4 mM Ca^{2+} in a simulated seawater medium. Inorganic carbon uptake and conversion within the cell led to increased medium pH which in turn led to the nucleation and eventual precipitation of CaCO_3 from solution as well as binding to the glass wall of the microcosm vessel. Results showed that substantial amounts of CaCO_3 were generated during the experiments; 3.1 and 1.7 mg CaCO_3 /day for *Synechococcus* sp. strain PCC 8806 and *Synechococcus* sp. strain PCC 8807, respectively.

On a practical basis; assuming an average whiting area in the ocean of 70 km² and an ocean depth of 5 m, *Synechococcus* sp. strain PCC 8806 could potentially precipitate up to 2.5 x 10¹² g of CaCO_3 per year. Assuming a 1:1 molar ratio between CaCO_3 and CO_2 utilized in the reaction, a sustained 70 km² whiting event by this organism could sequester over half the CO_2 produced by a 500 MW power plant in a year. CaCO_3 production by *Synechococcus* sp. strain PCC 8807 was roughly half that demonstrated by PCC 8806. These results demonstrate the potential for sequestration of CO_2 through cyanobacterially-mediated CaCO_3 precipitation.

BACKGROUND AND INTRODUCTION

Ice cores from the Antarctic have indicated that atmospheric CO_2 concentrations have been steadily increasing for the past 250 years (1). Atmospheric CO_2 concentrations measured at the Mauna Loa Observatory in Hawaii indicate an increase from approximately 316 ppmv in March of 1958 to a high of 374 ppmv in December of 2004 (2) Anthropogenic CO_2 emissions have increased by an average of 1.2% per year during the past 12 years with estimated emissions for 2002 reaching 5.8 billion metric tons of CO_2 (1). Microbial-based technologies, specifically those utilizing photoautotrophs, represent a promising solution for long-term CO_2 sequestration.

Much of the carbon that is represented in the global carbon cycle is sequestered (for the most part permanently) primarily as calcium and calcium-magnesium carbonates (3). In many cases, the carbonates are of biogenic origin, some precipitated by bacteria, cyanobacteria, and fungi. Calcium or calcium-magnesium carbonates are precipitated by numerous mechanisms, one of which is photo- and chemosynthetic autotrophy in the presence of Ca and Mg counterions.

Factors important in CaCO_3 precipitation are: (1) calcium concentration; (2) dissolved inorganic carbon (DIC) concentration; (3) the pH of the growth environment; and (4) the availability of nucleation sites for the formation of CaCO_3 (5). Microbes facilitate these processes by creating alkaline environments and increasing concentrations of DIC through their physiological activity (See Figure 1).

BACKGROUND AND INTRODUCTION (Cont.)

Oxygenic photosynthetic bacteria classified as cyanobacteria are important to the formation of carbonated sediments because they are common in freshwater bodies, such as the Great Lakes, and the cyanobacterium, *Synechococcus*, contributes up to 50% of chlorophyll a biomass in oligotrophic oceans (4). In addition, marine cyanobacteria are responsible for an estimated 20 – 40% of carbon fixation in oceans (5). Previous research in our laboratory indicated that nine out of nine strains in the genera *Synechococcus* and *Synechocystis* were able to calcify (6). As pH in the growth medium increased to near the second equilibrium constant ($pK_2 = 9.3$; seawater) (7) of CO_3^{2-} , soluble calcium decreased. Two of the strains, *Synechococcus* sp. strain PCC 8806 and *Synechococcus* sp. strain PCC 8807 were able to calcify to an extent that caused precipitation of CaCO_3 (6). Both organisms increased the pH in the growth medium faster than the other strains tested; thereby, facilitating formation of CaCO_3 sooner in the experiment.

The purpose of this study was to determine the capacity of PCC 8806 and PCC 8807 to remove CO_2 as CaCO_3 . To this end, the fate of calcium in the batch experiments was determined and the mass of CaCO_3 generated was determined.

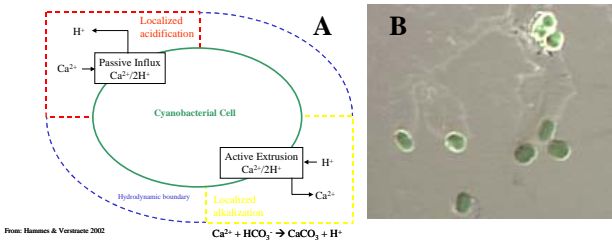


Figure 1. (A) Schematic showing the mechanism of CaCO_3 precipitation by cyanobacteria. (B) Photomicrograph of CaCO_3 encrusted cells.

MATERIALS AND METHODS

Batch Microcosms Studies:

- 500 ml serum vials
- 3.4 mM Ca^{2+}
- 2.5 mM HCO_3^-
- Starting pH ~8.0
- 12-hour light/dark cycle
- 28 $\mu\text{mol s}^{-1}\text{m}^{-2}$ of photon irradiance
- Growth temperature: 25 °C
- 0 mM HCO_3^- controls

Analyses:

- Carbon dioxide (Headspace-GC)
- pH
- Cell density (Direct Counts)
- Ca^{2+} (ICP-AES)



RESULTS AND DISCUSSION

❖ *Synechococcus* PCC 8807

- Cell density increased initially and then decreased as cells were encased in CaCO_3 .
- Growth medium pH remained stable for initial 3 days and then increased drastically between days 3 and 6.
- Ca^{2+} removal started after growth medium pH increased.
- CaCO_3 production appeared to be terminal process.

❖ *Synechococcus* PCC 8806

- Cell density increased gradually over course of experiment.
- Growth medium pH increased immediately.
- Ca^{2+} removal was continuous over duration of experiment.
- CaCO_3 appeared to be sustainable process over time.

❖ Control

- Initial increase in cell density but stabilized after day 3.
- Growth medium pH stabilized near 8.
- Ca^{2+} concentration remained stable over duration of experiment.

❖ Ca^{2+} partitioning

- Solid-phase Ca^{2+} in cell pellet and on surface of vessel.
- More Ca^{2+} in microcosms containing cells compared to controls.
- Maximum Ca^{2+} precipitation demonstrated by PCC 8806.

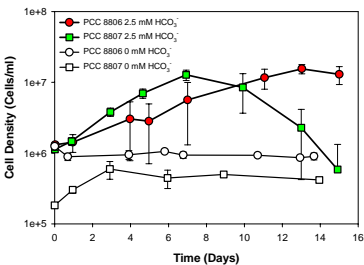


Figure 2. Cell density over time for cyanobacterial cultures receiving 2.5 mM HCO_3^- and 3.4 mM Ca^{2+} .

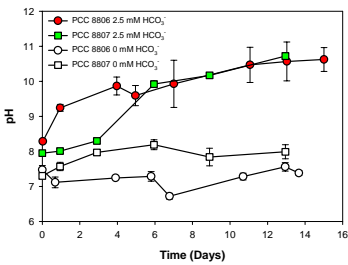


Figure 3. Effect of cyanobacterial growth on growth medium pH.

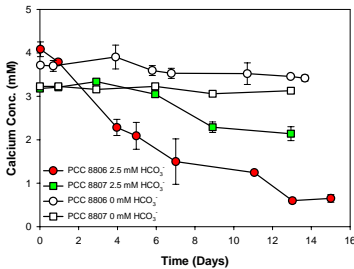


Figure 4. Calcium removal by cyanobacterial cultures.

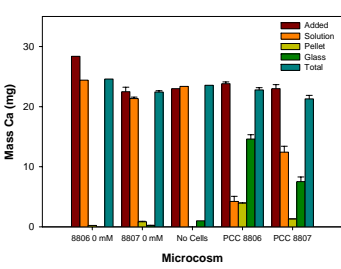


Figure 5. Distribution of calcium in microcosm experiments.

Table 1. CaCO_3 Production Potential by *Synechococcus* sp. strain PCC 8806 and *Synechococcus* sp. strain PCC 8807.

Assumptions for CaCO_3 Production:			
Average water depth (m)	5		
Average area of bloom (km ²)	70		
Yearly volume of bloom (m ³ /yr)	1.3 x 10 ¹¹		
	Total CaCO_3 precipitated (mg)	CaCO_3 precipitated/day (mg)	Mass of CaCO_3 per year (g/yr)
PCC 8806	18.6	3.1	2.5 x 10 ¹²
PCC 8807	8.9	1.7	1.4 x 10 ¹²



Figure 6. Whittings events; Andros Island, Bahamas

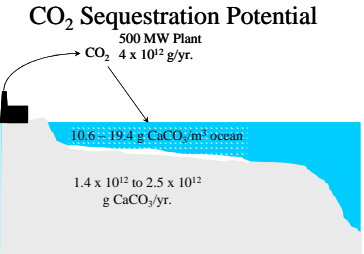


Figure 7. Carbon dioxide sequestration potential of using cyanobacterial precipitation of CaCO_3 .

CONCLUSIONS

- ❖ CaCO_3 precipitation by these species of *Synechococcus* appears to be controlled by continuous (PCC 8806) and discontinuous (PCC 8807) mechanisms.
- ❖ Greater than half of the CO_2 produced from 500 mW power plant could be sequestered as CaCO_3 by the continuous precipitation mechanism.
- ❖ Cyanobacterially mediated sequestration of CO_2 via precipitation of CaCO_3 appears to be feasible.

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